



## **HB21-1189 Community Monitoring: Quarter 2 2023**

### Scope and Applicability

To fulfill the community monitoring requirements outlined in The Regulate Air Toxics Act (HB21-1189), the Air Pollution Control Division (APCD) Air Toxics and Ozone Precursors Program (ATOPs) utilized the Community Air Toxics (CAT) mobile laboratory in accordance with the state of Colorado, Department of Public Health and Environment (CDPHE) mission. The CAT was designed and developed by ToFwerk and includes three instruments incorporated into a Mercedes Sprinter van for “real-time” measurement of ambient air while driving in communities. A duplicate of the CAT mobile lab, called the Emissions Monitoring Utility (EMU), was put into service on *December 8, 2023*.

The Colorado Regulate Air Toxics Act specifies monitoring of three toxic trace gasses (benzene, hydrogen cyanide, and hydrogen sulfide) in the communities surrounding four covered facilities to better understand how people in those communities are impacted by air quality. These air toxics are pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. HB21-1189 also directs Colorado’s Air Quality Control Commission to identify additional covered air toxics over time. This mobile monitoring platform allows for measurement of hydrogen cyanide, hydrogen sulfide, benzene, and several “non-covered” volatile organic compounds (VOCs).

### Method Overview

The CAT and EMU mobile laboratories both consist of two mass spectrometers and one optical spectrometer. Ambient air is introduced to the instruments through tubing on the roof of the van by an integrated mass flow controller. In addition, a MaxiMet weather station collects location, and meteorological data (temperature, pressure, wind speed and direction).

The Vocus Eiger Proton-Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) instrument operates using proton-transfer reaction mass spectrometry. This process uses hydronium ions ( $H_3O^+$ ) to measure volatile organic compounds (VOCs). In the first step, the primary (or “reagent”) ions react with trace gasses in air, ionizing them. The resulting analyte ions are separated and quantified with a time-of-flight mass spectrometer.

The Vocus Aim Chemical Ionization Time-of-Flight Mass Spectrometer (CI-ToF-MS) instrument operates using chemical ionization mass spectrometry. This is a two-step ionization technique. In the first step, the primary (or “reagent”) ions are made by illuminating a reagent gas stream with a vacuum ultraviolet lamp (VUV). The resulting ions are mixed with ambient air in a reaction cell. There, the reagent ions interact with trace gasses in air, ionizing them. The resulting analyte ions are separated and quantified with a time-of-flight mass spectrometer.

The Picarro Cavity Ring-Down Spectrometer (CRDS) analyzer uses light from a single-frequency laser that enters a cavity where three mirrors reflect the laser light. When the laser is on, the cavity quickly fills with laser light. A small amount of the laser light is transmitted through the mirror closest to the photodetector, which turns the incident light into a

signal that is directly proportional to the light intensity in the cavity. As the light circulates in a cavity with a gas sample, the molecular absorption by the gas results in a decrease of the light intensity. Plotting the absorbance at each measured wavelength generates an optical spectrum. This spectrum contains absorbance peaks that are unique to each molecule in the sample. The height of a particular absorption peak is proportional to the concentration of a molecule that generated the signal.

<b>CAT/ EMU Instruments</b>	<b>Compounds reported</b>
Vocus Eiger PTR-TOF-MS	Benzene, Toluene, Xylene, Trimethylbenzene
Vocus Aim CI-TOF-MS	Hydrogen Cyanide (HCN)
Picarro CRDS	Hydrogen Sulfide (H <sub>2</sub> S)

## Quarterly Data Summary Notes for Q2 2023

### Relevant links:

- [Community Air Toxics Mobile Lab \(CAT\) Flyer](#)
- [CDPHE- Regulate Air Toxics Act](#)
- Stationary Wind data resources:
  - [CDPHE Air Quality Dashboard](#)
  - [CDPHE Meteorology Data Selector Map](#)

### I. Limit of Detection and Method Detection Limit

Limits of Detection (LODs) were determined from auto-zeros the instrument performs during regular operation and these values change each time the instrument performs an auto-zero. LODs reported in the data summary are averaged quarterly from these moving LODs. All LODs used in flagging the data are reported on the “LOD” sheet. The reported Method Detection Limits (MDLs) were determined during the instrument audits. The table of LODs and MDLs for each compound and asset are reported on the Quarterly Summary tab of the Data Summary.

All LODs used to flag data are reported on the LODs tab. If the LOD is “nan” (or blank) for a given compound and timeframe, or if a given timeframe is missing altogether, then the MDL was used to flag the data instead. The “MD” flag was used to flag non-negative data that is less than the LOD or MDL. The moving LODs are computed as 3 times the standard deviation of auto-zeros that the instrument(s) perform during normal operation.

### II. Computing Statistics

Data with the flag “BR” (indicating negative values) are replaced with zeros for computing statistics and non-zero data that are flagged “MD” are replaced with  $0.5 * MDL$  for statistics.

The quarterly pollutants stats table was computed at the end of the quarter for the specific region.

### III. Instrument Time Delay

There are sampling time delays between the different instruments due to differences in sample line tubing length and sampling flow rates. Currently, this time delay is not corrected for in the

quarterly data packets. These sampling delays were measured directly during the audits and were determined from bump tests at the inlet lines located at the top of the van.

<b>CAT Instruments</b>	<b>Compounds reported</b>	<b>Time Delay of sampling (CAT)</b>
Vocus EIGER PTR-ToF-MS	Benzene, Toluene, Xylene, Trimethylbenzene	6.5 seconds
Vocus AIM CI-ToF-MS	Hydrogen Cyanide (HCN)	7.5 seconds
Picarro CRDS	Hydrogen Sulfide (H <sub>2</sub> S)	9 seconds

#### **IV. Meteorological Data**

A large amount of MetData has the flag “QW”, indicating questionable wind data.

When the vehicle is moving quickly and wind speeds are low, it can be challenging to accurately measure true wind.

Wind data are flagged if:

1. True wind cannot be distinguished from the wind generated by the vehicle’s motion while driving.
2. The difference between the wind speed (direction) and the vehicle’s speed (direction) is less than the error of the MaxiMet.

If the MetData are flagged “QW”, we encourage the user to use external sources to verify wind speed and direction:

[CDPHE Air Quality Dashboard](#)

[CDPHE Meteorology Data Selector Map](#)

#### **V. Quarter Specific notes**

##### **A. Limit of Detection**

Routine LOD determination was not performed until later quarters and therefore no LOD data is reported under the LOD tab for Q2 2023. Only MDL data was used for the “MD” (values less than MDL) flag for Q2 2023.

##### **B. VOCUS AIM CI-ToF-MS Instrument Downtime**

The Vocus AIM CI-ToF-MS was not operational during April 2023 due to non-routine instrument maintenance attributed to a pump failure. Due to instrument downtime, no HCN measurements were acquired in April 2023. The Vocus AIM CI-TOF-MS pump was replaced at the end of April 2023 and operational at the start of May 2023.

### **C. Elevated background in Eiger and AIM**

The quality control and assurance procedures for the Community Air Toxics (CAT) mobile lab were in their development phase during the first year of sampling in 2023. A previously unknown issue of inlet line contamination was discovered on September 20, 2023 after reviewing quarterly data and a physical inspection of the inlet lines which confirmed the presence of visible residue.

It was determined that the sample inlet lines were contaminated due to gradual particle deposition. This inlet contamination is suspected to have started in the second quarter of sampling on approximately April 26, 2023, based on elevated daily average concentrations of the target compounds, resulting in elevated quarterly averages for compounds detected via PTR-ToF-MS and CI-ToF-MS (benzene, toluene, xylene, trimethylbenzene, and hydrogen cyanide). Currently, this is not corrected for in the data, as the exact contribution to elevated concentrations from gradual sample line contamination cannot be determined.

After this issue was discovered, sampling inlet lines were replaced on September 20, 2023 and monthly averages of target compounds decreased. As a result of this issue, quality control and assurance steps were put into place to minimize this occurrence and identify this problem more quickly in the future.